

SUPPLEMENTARY MATERIAL

Phosphorus losses from agricultural land to natural waters are reduced by immobilization in iron-rich sediments of drainage ditches

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1. Study sites

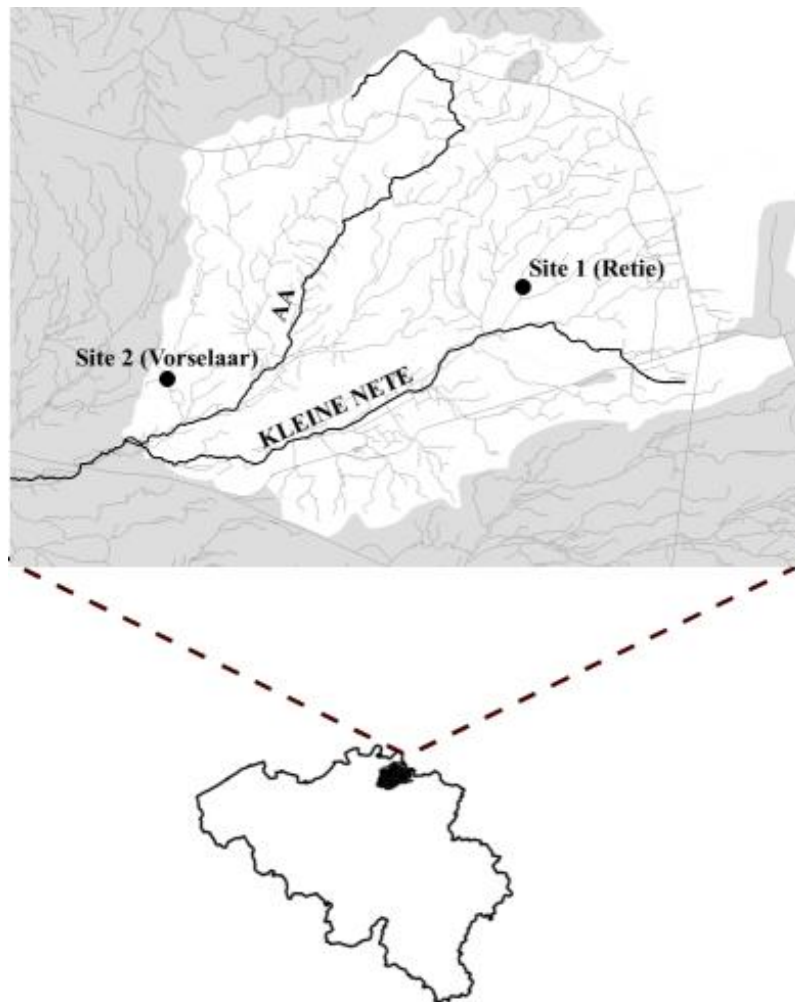
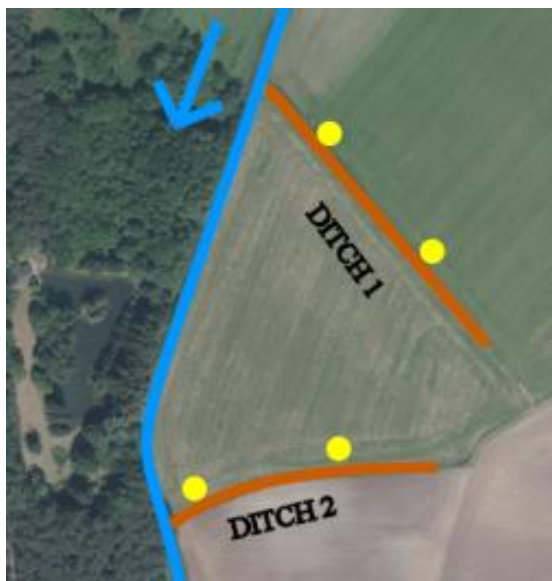


Figure S 1: Map of Belgium with the Kleine Nete catchment and the study sites indicated.



Site 1 (Retie)



Site 2 (Vorselaar)



Ditch 2



Ditch 3

Figure S 2: Bird's-eye views and pictures of the sampling sites. The ditches are indicated in reddish brown, the groundwater monitoring wells in yellow, and the streams and their flow direction in blue.

2. Details of the DET method

The assemblage and pretreatment of DET probes were performed as described previously (Davison et al., 1994). A hydrous polyacrylamide gel was cast by pipetting a gel solution between two glass plates separated by a plastic spacer (thickness 0.6 mm) and by allowing it to polymerize at 45°C for 1 hour. After hydration of the gels in ultrapure water, the thickness of the gels was determined by microscopy and was 0.94 ± 0.05 mm. The gels were cut to the correct dimensions and were assembled into plastic sediment-DET probes (DET Research Ltd., Lancaster, UK). A 0.45 µm nitrocellulose membrane filter (Whatman Protran BA 85) was placed on top of the gel layer in order to exclude particulates. The probes were deoxygenated overnight in sealed bottles containing 0.01 M NaCl by purging with N₂. The probes were removed from the sealed containers in the field and immediately deployed by gently pushing them into the sediment until approximately half of the probe was below the sediment-water interface. After 24 hours, the probes were retrieved, rinsed with ultrapure water, and immersed in a 0.01 M NaOH solution within 10 s. The NaOH causes fast oxidation of Fe(II) and subsequent precipitation of Fe as oxyhydroxides. The formed Fe hydroxides are thereby immobilized because they are too large to move due to the cross-linking of the polyacrylamide chains in the gel (Davison et al., 1994). In this study, this method was used for the first time to also measure P, since P can quantitatively be bound by Fe oxyhydroxides as long as Fe occurs in molar excess (see below). Upon return to the lab, the probes were disassembled, and the gels were cut to 1-cm slices. The Fe and P were re-eluted from the gel by immersing each slice in 1 mL of 1 M HCl for 24 hours. Afterwards, the gels were removed, the eluates were diluted to 5 mL, and the concentrations of Fe and P were measured by ICP-MS. The detection limits of the ICP-MS were around 3 µg P L⁻¹ and 1 µg Fe L⁻¹; after accounting for the dilution factors, the detection limits in DET sampled sediment pore waters were around 0.1 mg P L⁻¹ and 0.03 mg Fe L⁻¹.

3. Sediment cores

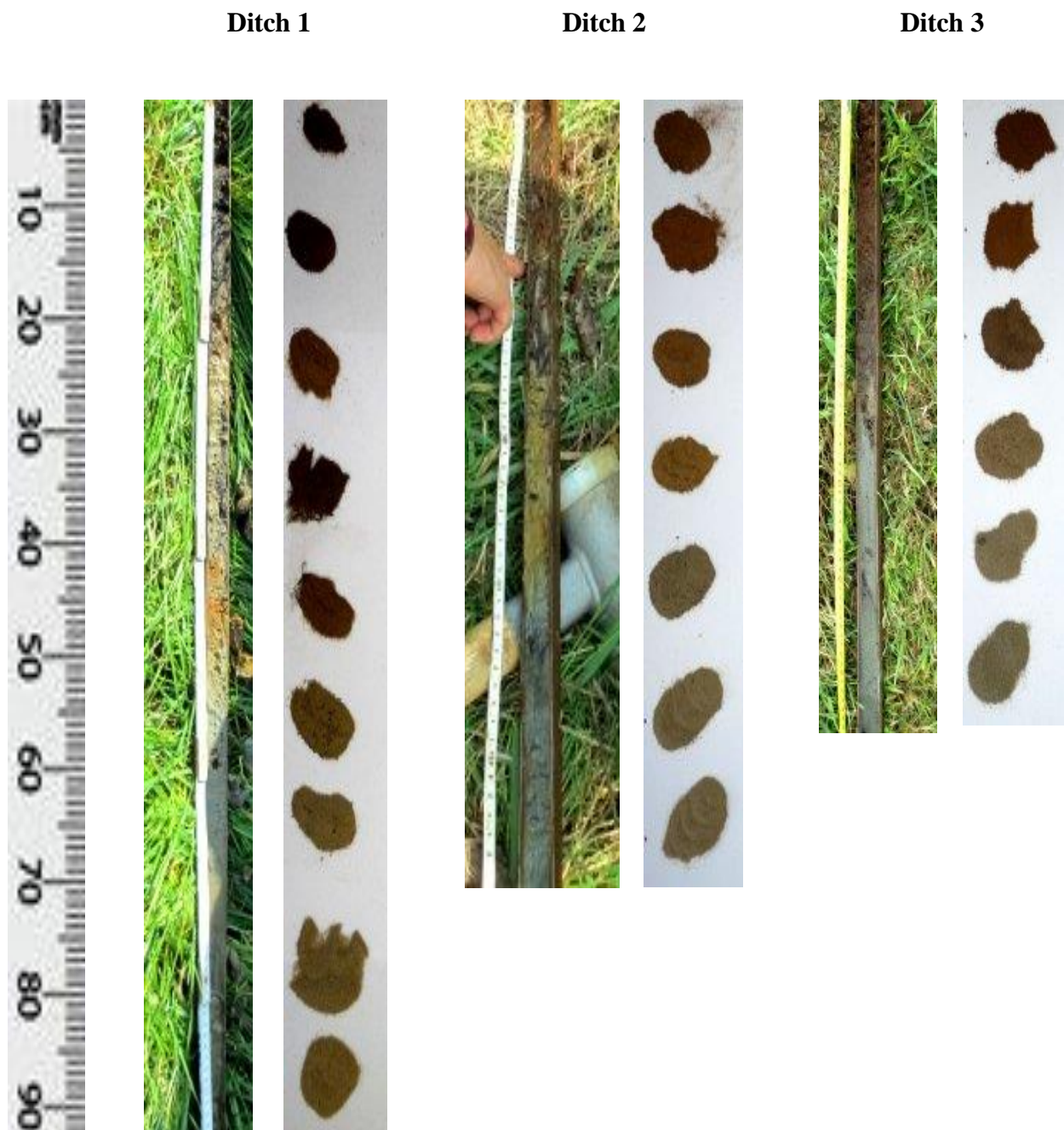


Figure S 3: Fresh cores (left) and dried samples (right) of ditch sediment and of the underlying parent material. The scale bar indicates the approximate depth (in cm) below the surface of the ditch sediment.

Table S 1: Oxalate extractable concentrations of Al, Fe, Mn and P, their molar ratio, the P sorption capacity (PSC), and the degree of P saturation (DPS) in cores of the ditch sediment and the underlying parent material.

	depth <i>cm</i>	Al	Fe <i>mmol kg⁻¹</i>	Mn	P	Al:P	Fe:P	Mn:P	PSC <i>mmol kg⁻¹</i>	DPS %
DITCH 1	0-10	36	248	0.2	44	0.8	5.6	0.00	142	31
	10-20	19	81	0.1	15	1.3	5.5	0.01	50	30
	20-30	11	50	0.2	6	1.7	7.9	0.02	30	21
	30-40	23	75	0.1	13	1.7	5.8	0.01	49	26
	40-50	14	36	0.1	5	2.7	7.0	0.02	25	21
	50-60	8	7	0.1	1	9.4	9.3	0.12	8	11
	60-70	6	5	0.1	1	10.2	8.8	0.19	6	11
	70-80	4	3	0.1	0.5	9.3	7.1	0.16	4	12
	80-90	6	6	0.1	1	8.0	7.6	0.12	6	12
DITCH 2	0-10	27	220	0.5	16	1.6	13.3	0.03	123	13
	10-20	31	232	0.4	19	1.6	12.3	0.02	131	14
	20-30	18	112	0.2	9	2.0	12.5	0.02	65	14
	30-40	7	44	0.2	2	3.7	23.4	0.08	26	7
	40-50	7	27	0.1	1	6.1	23.9	0.13	17	7
	50-60	5	23	0.1	1	5.4	24.0	0.11	14	7
	60-70	4	16	0.1	1	4.9	18.0	0.10	10	9
DITCH 3	0-10	18	1958	2.8	142	0.1	13.8	0.02	988	14
	10-20	16	1205	1.2	137	0.1	8.8	0.01	610	23
	20-30	7	166	0.2	24	0.3	7.0	0.01	86	27
	30-40	2	24	0.03	3	0.8	8.7	0.01	13	21
	40-50	3	5	0.05	1	2.1	3.5	0.03	4	36
	50-60	4	7	0.04	1	4.0	7.3	0.04	5	18

4. Concentration profiles of Fe and P

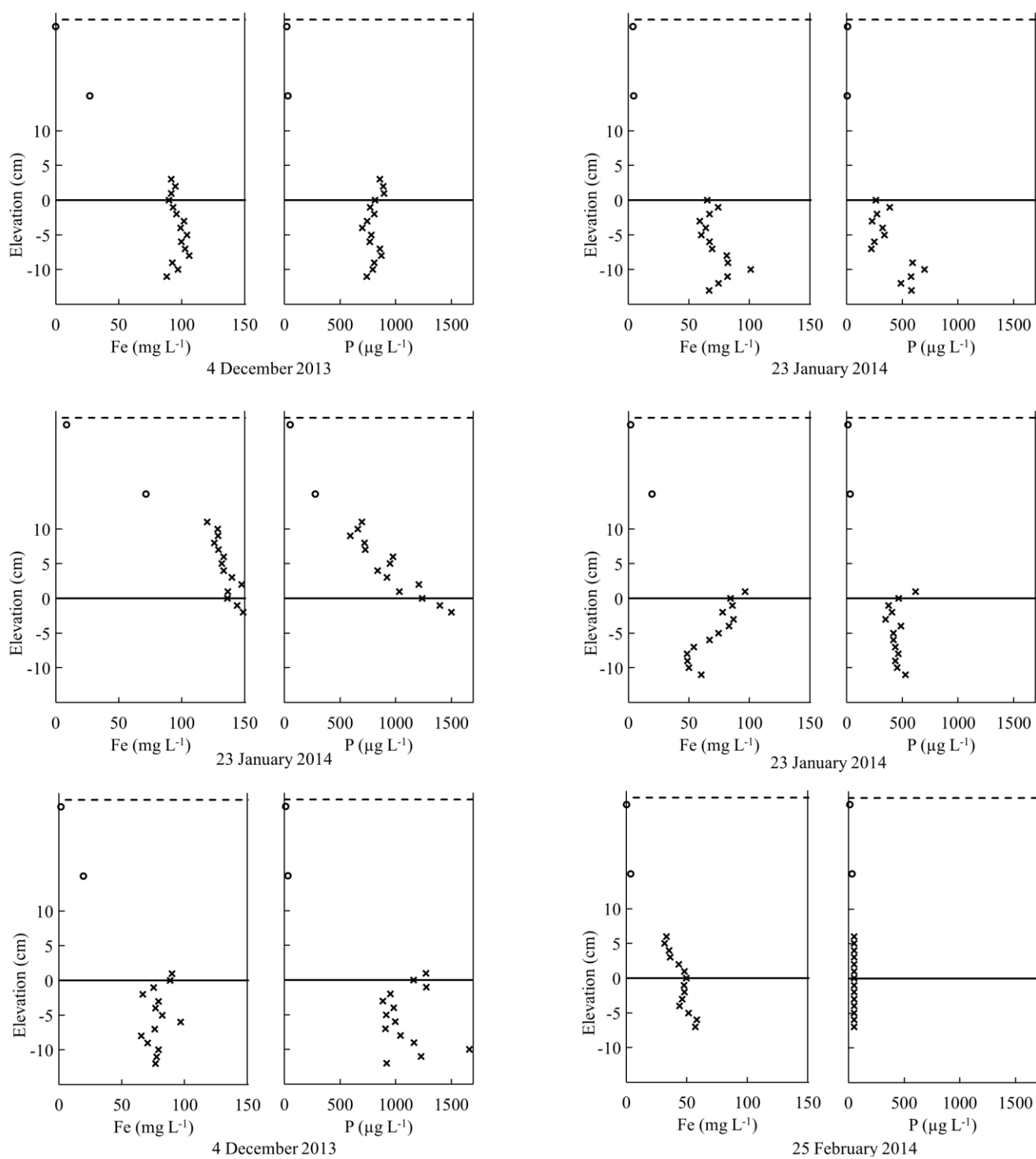


Figure S 4: Concentration profiles of Fe and P in the sediment pore water and in the overlying water layers of ditch 1. Open circles refer to water samples taken with a syringe either 1 or 10 cm below the water surface; crosses refer to concentration profiles determined by diffusive equilibration (DET). Some data points were below the detection limit of the DET method for P (100 μg P L⁻¹) and are plotted at 50 μg P L⁻¹. The full line is the water-sediment interface, the dashed line is the water surface. The sampling date is shown below each concentration profile.

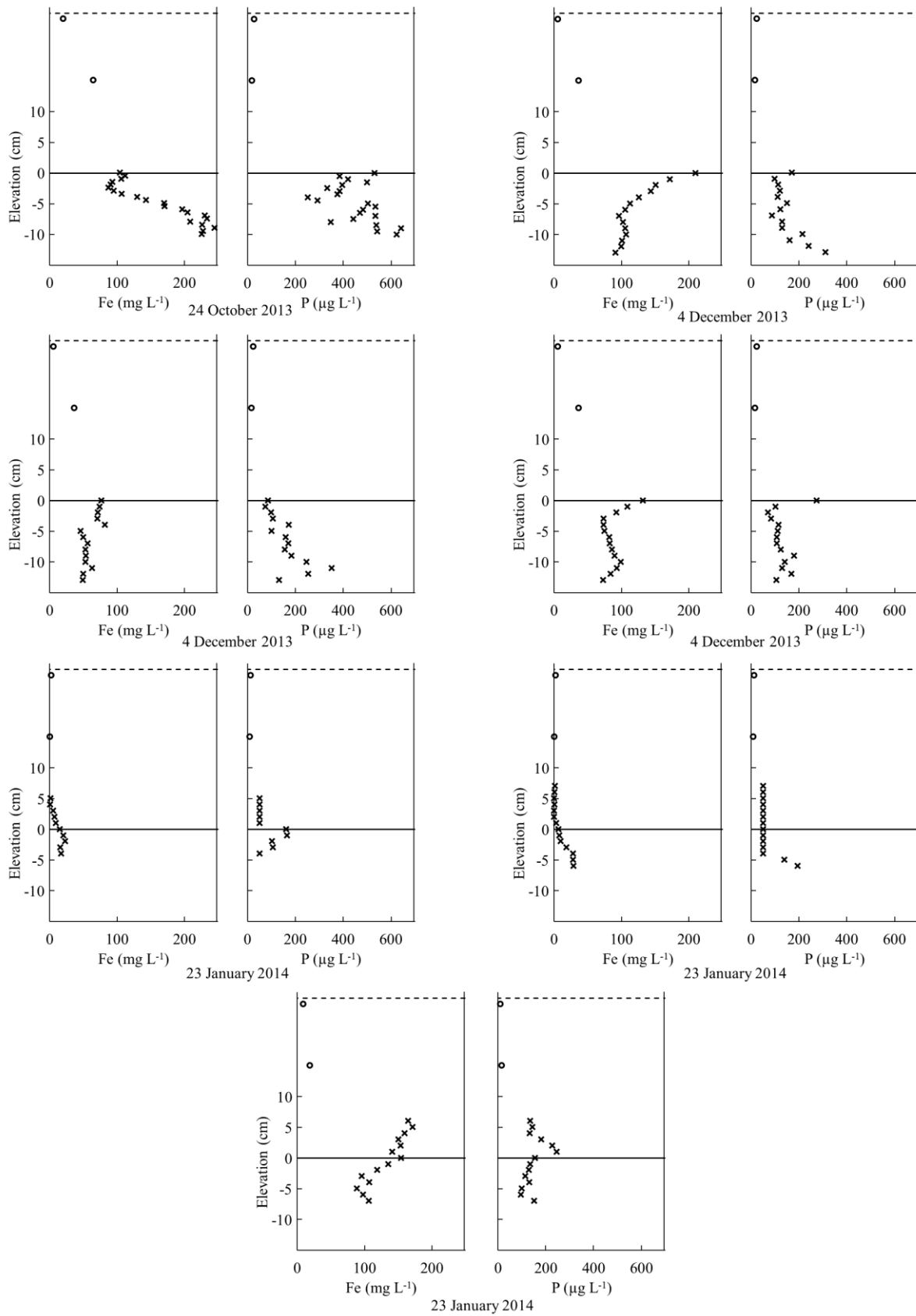


Figure S 5: Concentration profiles of Fe and P in the sediment pore water and in the overlying water layers of ditch 2.

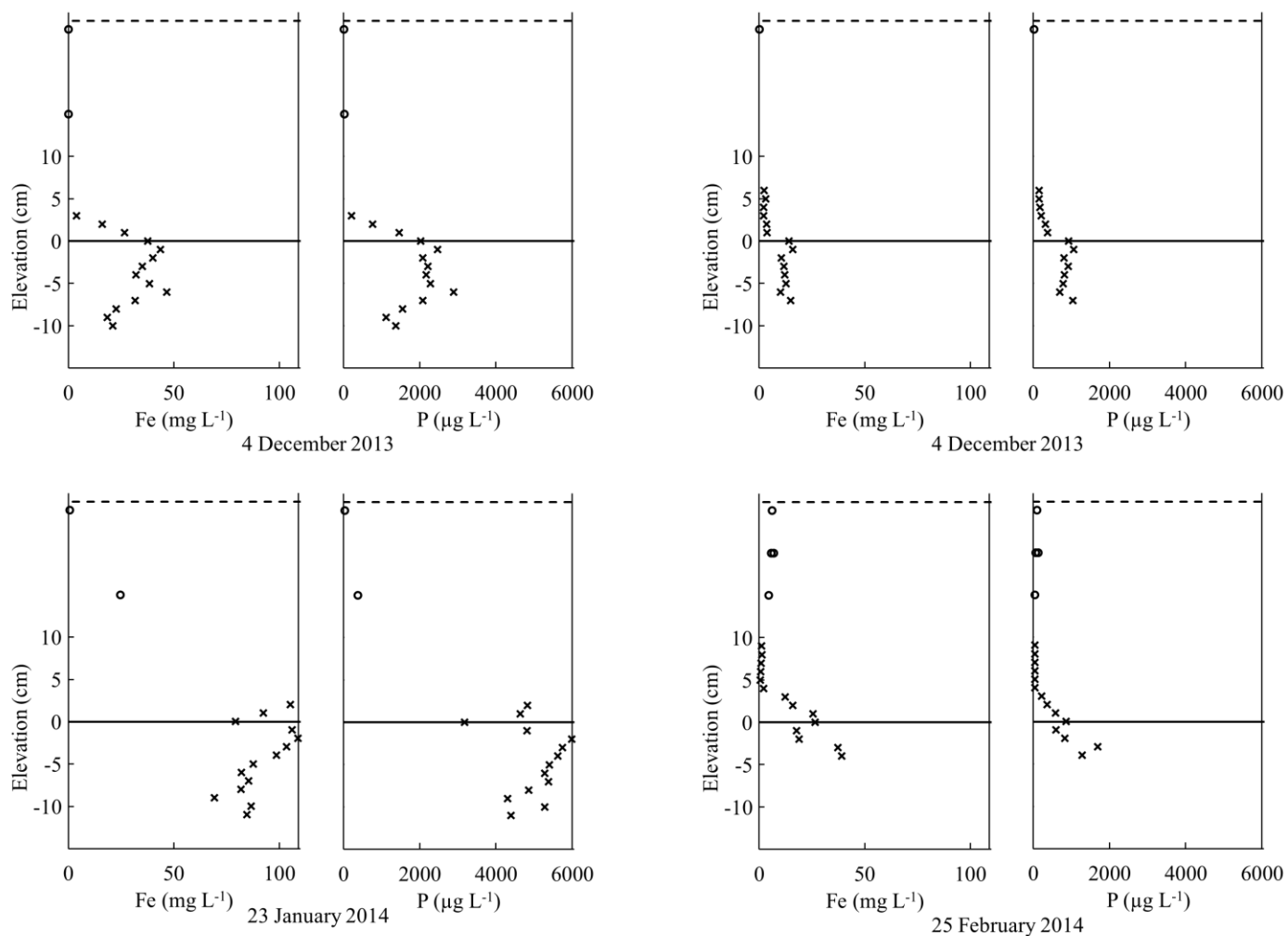


Figure S 6: Concentration profiles of Fe and P in the sediment pore water and in the overlying water layers of ditch 3.

5. References

Davison, W., Zhang, H., Grime, G., 1994. Performance characteristics of gel probes used for measuring the chemistry of pore waters. *Environ. Sci. Technol.* 28, 1623–32.